

# **Modeling of Natural Remediation: Contaminant Fate and Transport**

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Predictive models can play an important role in verifying the occurrence and significance of natural remediation and can significantly improve the design of monitoring and assessment procedures. Predictions resulting from the models can be used to address important questions that invariably arise during the assessment of remediation by intrinsic processes. Such questions may include the following: “Will environmentally important receptors be impacted by the contaminant?; What are the expected average and maximum concentration levels and what is the associated risk?; How long will it take for the contaminant plume to degrade below regulated limits?” To answer these questions, one must adequately describe the key natural remediation processes that are active at the site. To accomplish such description, robust mathematical models capable of predicting the transport and reaction of contaminants are required.

Typically, models used to evaluate natural remediation modeling involves two distinct modeling steps: 1) modeling the general environmental system (e.g., sediment, surface water, and/or groundwater) and 2) modeling the transport and reaction of specific contaminants. Interactions between contaminants and environmental materials often control the rates of natural remediation. Partitioning of fuel hydrocarbons to soil organic matter can limit the rate of hydrocarbon transport and also the rate of bacterial degradation. The interactions might be sufficiently important that they may modify the properties of the system itself. One case where interactions of this type can be important is when rapid microbial growth during an in situ bioremediation effort might significantly reduce the permeability and porosity of the porous media (Taylor and Jaffe, 1990; Clement et al., 1996b). However, for most natural remediation modeling applications, the flow and reactive transport may be considered as uncoupled processes.

For complex environmental systems such as those typically encountered at contaminated sites, computer models will never give answers that accurately reflect all aspects of the complex chemical and microbial interactions that may be occurring. For natural remediation, rather than giving “answers”, models should be used to predict future trends and to provide insight into the relative importance of various processes that are occurring at the site. In this way, a natural remediation model can be used as a project mentor, rather than as a project director. Complex models such as these are subject to many conditions that may severely limit the accuracy or applicability of a particular model to a particular site. These limitations may or may not be known at the time the natural remediation assessment begins. During an initial site characterization, for example, based on limited data, a model can be used to predict the order of magnitude of the contaminant plume distribution and give rough estimates for various rates of degradation and dispersion. This information can be very useful when designing a site characterization plan or estimating initial sampling costs. Data obtained in the initial phase of the site characterization can be incorporated into the model to improve predictions regarding the rate of plume movement from the initial contaminating event to the current volumetric extent of the contamination. Time-phased sampling events may be used to calibrate the temporal aspects the model to allow predictions of future extent of contaminant spreading, rates of natural remediation, and the eventual decline and disappearance of the contaminant.

For evaluation and acceptance of natural remediation as a viable treatment option, the value of models to predict long-term risk cannot be overemphasized. In addition, a carefully assembled and validated model can help address stakeholder and regulator concerns over the rate and extent of contaminant movement. Models are important tools with which to provide valuable insight

into the complex systems that bring about the natural remediation of contaminants. The goal of this chapter is to provide a basis of understanding of the appropriate issues important for modeling natural remediation of contaminants in both surface water and groundwater.

## **5.1 Surface Water Biogeochemical Transport Models**

Surface water biogeochemical models describe the movement of water and sediments in relation to the transport and transformation of contaminants. These models can be valuable tools in the evaluation of natural remediation of contaminants in aquatic ecosystems. Typically, surface water biogeochemical transport models have three coupled components as illustrated schematically in Figure 6-1: hydrodynamics; sediment transport; and contaminant fate. The hydrodynamics component involves the movement of water and the friction or shear that this movement causes at the interface between the water and the sediment bed. A hydrodynamic model computes the velocity and depth of the water column, as well as the shear stress at the water-bed interface, in response to upstream flows and flows entering from tributaries or the downstream boundary. The sediment transport component includes the movement of suspended and settled solids with the moving water and the settling and resuspension of solids that occurs at the water-sediment interface as a result of the shear caused by the moving water. A sediment transport model computes the concentration of solids in the water column and the rate at which sediment accumulates in the bed. The contaminant fate component includes the transport of contaminant dissolved in the water or sorbed to solids, the transfer between the dissolved and sorbed state, the transfer among chemical species of the contaminant, the transfer between the water and the atmosphere, and the degradation that occurs because of biotic or chemical reactions.

A contaminant fate model computes the concentrations of the contaminant in the water column and in the sediment. The models used to assess natural remediation are systems of equations developed from the basic principles of conservation of mass, energy and momentum, equations of state, and laboratory and field studies of individual phenomena. These equations are general and can be applied to various surface water systems. The application of the equations to a specific system involves the determination of appropriate values for each of the parameters in the equations. Site-specific data are the basis for assigning values, either directly or by the process of model calibration. Each of the three models must be calibrated and validated using the available data. Good site specific data are the key to the accurate prediction of natural remediation; if these data are not available, the utility of model predictions may be limited. Nevertheless, in the absence of high quality data, modeling can still be instructive for identifying critical processes and future data collection needs.

A number of biochemical transport modeling approaches are in use. However, only a few of these approaches are appropriate for addressing natural remediation. Because fundamental questions regarding natural remediation often require the assessment of either the rate of contaminant decline or the time to achieve some endpoint, steady-state models are inappropriate. Because natural remediation in surface water systems is invariably a function of cyclic or event-related phenomena such as temperature, light, flow and solids loading, models that assume temporally constant rates of input or reaction are inadequate (Connolly 1997). A widely-used framework that does not suffer these limitations is WASP (Ambrose et al. 1993). This framework utilizes a flexible compartment modeling approach that can represent a surface water

in one, two or three dimensions. The hydrodynamic and sediment transport components are separate from the fate component, allowing for convenient modification of the fate component to include reaction processes unique to the contaminant being modeled. The WASP modeling framework, or a variant of it, has been applied to evaluate natural remediation in the lower Fox River (Vellueux et al. 1995), Green Bay (Raghunathan et al. 1994), the James River (O'Connor et al. 1989) and the Hudson River (Thomann et al. 1991). The primary limitation of this WASP-like frameworks is that hydrodynamics and sediment transport are uncoupled. Rates of erosion and deposition, input in the form of settling and resuspension velocities, are independent of input rates of flow and velocity. This limitation can be overcome by using a hydrodynamic-sediment transport model (e.g., TABS-2; Thomas and McAnally 1985; SEDZL; Ziegler and Nisbet 1994) to calculate a time series of erosion and deposition rates from a time series of flows which serve as inputs to the fate model.

### **5.1.1 Use of Models to Assess Natural Remediation in Surface Water Ecosystems**

Assessment of natural remediation in surface waters often focuses on the reduction in contaminant concentration in surface sediments. Here surface sediments refers to sediments from which contaminants are potentially available to biota. Natural remediation in surface water ecosystems is the cumulative result of reaction processes that destroy the contaminant, transfer processes that move the contaminant between the sediment and the water column and between the water column and the atmosphere, and sedimentation that buries and dilutes the contaminant (Figure 6-1). Data must exist on all of these processes in order to have confidence in model predictions.

Often the primary mechanism of natural remediation in surface waters is burial of contaminated sediments by relatively clean sediments (Michelson 1999). Most of the solids loading responsible for burial typically enters the system in short term events that occur only a few times each year (Ager 1981). Accurate estimation of the relationship between flow and solids loading and simulation of sediment transport during the event periods is necessary for accurate prediction of burial rate and contaminant fate (Ziegler and Connolly 1995; Cardenas and Lick 1996). A practical example of this postulate is found in a model of the natural remediation of Kepone in the James River estuary (O'Connor et al. 1983; 1989). The first version of this model assumed constant flow at the annual mean. This version significantly over predicted the rate of decline of sediment Kepone concentrations. By modifying the model to account for flow variation and the variable solids loading, the predicted rate of decline agreed with the observed rate.

### **5.1.2 Current State of the Art**

All of the physical, chemical and biological processes that determine the fate of a contaminant in a surface water system have been the subject of extensive scientific investigation that has allowed the development of sophisticated models. However, the information requirements of these models are formidable and their computational requirements can be extreme. Consequently, aggregation of these models into a biogeochemical transport model remains beyond the current state-of-the-art. Biogeochemical transport models have tended to use relatively simplistic descriptions of some or all of the components. The structure and application of the state-of-the art component models that comprise a biochemical transport model are reviewed below.

### 5.1.3 Hydrodynamics

Hydrodynamics are described by two and three-dimensional models that account for the major forces affecting water motion. These forces include horizontal pressure gradients associated with the slope of the water surface (due to channel slope, tides and/or seiches), internal density gradients (due to salinity or temperature gradients), wind stresses at the water surface, bottom stresses at the water-bed interface, internal friction or viscosity and Coriolis acceleration (important only in coastal waters and oceans). The accuracy of the hydrodynamic calculation typically depends on the scale of the numerical grid, the resolution and accuracy of bathymetric data and boundary forcing functions (stage height, salinity, wind speed and direction, tributary inflows), and the availability of sufficient current, temperature, salinity (if an estuary or coastal water) and water surface elevation data within the system to allow accurate estimation of bottom friction factors or equivalently bottom roughness heights.

The approach used to calibrate a hydrodynamic model is dependent on the available data. Typically, the bottom friction factor is adjusted to maximize the fit between computed and observed values of water surface elevation and current velocity data. The approach is illustrated by two examples. Quantitative Environmental Analysis, LLC (1999) calibrated hydrodynamic models for each of eight dammed reaches of the Upper Hudson River by fixing the dam stage height at the downstream limit of the model at the measured value and then adjusting the bottom friction factors until good agreement was achieved between the predicted and measured stage heights at an upstream location. The models were validated by simulating a flood that occurred in May 1983 and comparing computed and observed stage height measurements (Figure 6-2).



HydroQual, Inc. (1998) calibrated a hydrodynamic model of Lavaca and Matagorda Bays on the Texas Coast. A fine scale numerical grid was employed with 5,280 horizontal elements and ten vertical layers used to describe the approximate 80 km<sup>2</sup> bay system. A time series of water surface elevations at the connection to the Gulf of Mexico, wind velocities and tributary inflows were used as forcing functions. The bottom roughness height was used as the calibration parameter. Calibration was assessed using a one-month time-series of water surface elevations at several locations within the bay system and current velocities measured at a single location in Lavaca Bay. A bottom roughness height of 0.6 mm yielded good results. The model predicted hourly water surface elevations at three locations with a mean error of 2% (Figure 6-3). Predicted current velocities also agreed well with observations (Figure 6-4).

#### **5.1.4 Sediment Transport**

Sediment transport is simulated using a simplification of the distribution of particle sizes in a surface water. Typically, suspendable sediments are aggregated into two classes; one representing fine grain (cohesive) particles with diameters less than 62 micrometers and the other representing fine sands with diameters between 62 and 250 micrometers (e.g., Ziegler and Nisbet 1994). Various empirical formulations exist to describe the deposition and resuspension of these particle classes. The parameters in these formulations are site-specific, particularly for resuspension, and require direct measurement (e.g., Tai and Lick 1986; Jepsen et al. 1997). In addition to the obvious importance of accurate characterization of deposition and resuspension, the accuracy of the solids loading measurements (or the flow-solids loading correlation) and the accuracy of the particle size distribution of that loading are important determinants of model

accuracy. In cases where the solids loading or the particle size distribution of that loading are poorly characterized, model calibration can result in incorrect estimates of the rates of resuspension and deposition. If solids loading is underestimated, calibration may result in too much solids resuspension to achieve the measured suspended solids levels. Further, it is likely that the burial rate would be underestimated and consequently, so would the rate of natural remediation. This difficulty occurred in a preliminary model for the Upper Hudson River (USEPA 1996). The solids loading for two tributaries were significantly underestimated, resulting in an overestimate of resuspension and the incorrect calculation of net erosion rather than net burial (Schweiger et al. 1996).

The development of a sediment transport model begins by defining the characteristics of the sediment bed. A bed map is constructed in which the bed is divided into a minimum of three classifications: cohesive sediments; non-cohesive sediments and hard bottom. The non-cohesive sediments may be further divided on the basis of median particle size. The erosion properties of the cohesive sediments are defined by measurement and those of the non-cohesive sediments are defined by specified values of an active layer depth and median particle diameter (Ziegler and Nisbet 1994). Tributary solids loading is defined by a data-based relationship between solids loading and tributary flow (e.g., Ferguson 1987; Walling and Webb 1988). Settling velocities of the cohesive sediment classes are defined by empirical correlations to particle size and concentration and water column turbulence (Ziegler and Nisbet 1995). The settling velocity of the non-cohesive particles is a function of particle size (Cheng 1997). The model is calibrated by comparison to total suspended solids (TSS) data during flood conditions (e.g., Ziegler and Nisbet 1994) and also by comparison of predicted and observed rates of sedimentation (e.g.,

Ziegler and Nisbet 1995). Calibration parameters include the particle size composition of the solids loading and the median particle size and active layer depth of the non-cohesive sediments.

The upper Hudson River hydrodynamic models discussed earlier were used with a sediment transport model to predict erosion and deposition of sediment and associated polychlorinated biphenyls (PCBs) (Quantitative Environmental Analysis 1999; Ziegler et al. submitted). Suspended solids data from an April 1994 flood were used to calibrate the model. Comparisons of predicted and observed TSS at four locations covering a 55 km length of river are presented in Figure 6-5. The model closely approximates the observed data at all of the locations. It captures both the temporal variation and the general increase in TSS concentrations through the 55 km between the Thompson Island Dam and Waterford.

### **5.1.5 Contaminant Fate**

Contaminant fate models combine the water velocity and resuspension/deposition results of the previous two components with descriptions of the reaction and intermedia transfer processes that affect a contaminant. The transfer processes include sorption, exchange between the atmosphere and the dissolved phase in the water column and exchange between the dissolved phase in the water column and the sediment bed pore water. The reaction processes include speciation, precipitation/dissolution and biotic and abiotic degradation.

Sorption is described as a reversible equilibrium process; most commonly by a partition coefficient. Laboratory experiments indicating relatively slow desorption rates (e.g., Pignatello and Xing 1996) or reductions in the bioavailability of sorbed contaminants with sediment aging

(e.g., Loonen et al. 1997) suggest that the assumptions of equilibrium and reversibility may be inaccurate. The significance of any inaccuracies has not been rigorously evaluated, indicating that this is an area of needed research. Nonetheless, reversible equilibrium has been used with some success for over twenty years.

Speciation is described using chemical equilibrium models such as MINTEQA2 (Allison and Perdue 1994), MINEQL<sup>+</sup> (Schecher and McAvoy 1995) and WHAM (Tipping 1994). These models provide accurate estimates of speciation and precipitation/dissolution of inorganics so long as the major chemical species in the water are well known and kinetic limitations do not influence speciation (i.e. thermodynamic equilibrium is assumed in these models). These models are computationally intensive and their use in long-term natural remediation simulations involves compromises between the frequency at which the speciation is updated and the accuracy of the solution. In addition, accurate application of these models to natural soils and sediments is quite difficult since calibration of contaminant binding to heterogeneous sites is not straightforward.

Chemical and biochemical reactions that create or destroy a contaminant of concern are described in simple fashion. A second-order kinetic expression is used in which the reaction rate is proportional to the concentration of the contaminant and the concentration of another reactant such as the hydroxyl ion or bacteria. In the case of a biological reaction, the organism responsible for the reaction is not modeled. An organism concentration is input to the model, either as a constant or as a time function. This also may be the case for a chemical reactant, if a chemical equilibrium model is not incorporated within the modeling framework.

Because the influence that site characteristics have on many chemical and biochemical reactions is not well understood (Boethling and Alexander 1979; Lartiges and Garrigues 1995), it is common to use simple first-order reaction rates that are defined from laboratory experiments or from model calibration (e.g., Dilks et al. 1993; Tell and Parkerton 1997). The accuracy of such descriptions is dependent on how well the model describes all other processes: the greater the number of parameters that must be adjusted during calibration, the more uncertain the model predictions.

A volatilization mass transfer rate constant is used to compute air-water exchange. It is calculated typically from empirical formulations dependent on the molecular diffusivity of the contaminant, water velocity, water column depth and wind velocity (e.g., Mackay and Yeun 1983; Rathbun 1990). The equations are fairly robust and yield accurate volatilization rates. The principal weakness of existing models is their inability to describe volatilization losses that occur at waterfalls. Such losses can be important for volatile chemicals (McLachlan et al. 1990).

Transfer at the water-bed interface refers to the movement of contaminant between the water column and the sediment pore water. The models describe this process using a diffusion equation. A number of phenomena affect the transfer, including: bioturbation; hydrodynamic pumping due to pressure gradients, and; advection to or from groundwater. As a result, the transfer rate is site-specific and varies temporally at a site (eg., Riedel et al. 1988; Gill et al. 1999). The diffusion model is an obvious simplification. In cases where water-bed transfer is an important mechanism, the accuracy of the model is dependent on the existence of data for calibration of this transfer rate constant.

The Hudson River model (Quantitative Environmental Analysis 199; Connolly et al. Submitted) is again used to illustrate model application. Daily values of river flow and water depth for the period from 1977 to 1991 were obtained from the hydrodynamic model. Rates of resuspension and deposition were obtained from the sediment transport model. The sorption partition coefficient was determined from an analysis of dissolved and particulate PCB measurements taken by the USEPA as part of a field data collection program (USEPA, 1997). A 20°C organic carbon normalized partition coefficient ( $K_{oc}$ ) of  $10^{5.6}$  L kg<sup>-1</sup> organic carbon was used in the model. The volatilization rate constant was calculated from two film theory using a Henry's Law constant of  $2 \times 10^{-4}$  atm-m<sup>3</sup> mol<sup>-1</sup>, a liquid film mass transfer coefficient calculated using the O'Connor-Dobbins reaeration equation and a gas film mass transfer coefficient fixed at 100 m day<sup>-1</sup>. The vertical diffusion of PCBs between the pore waters of adjacent sediment segments was modeled using a diffusion coefficient of 1 cm<sup>2</sup> day<sup>-1</sup>. A time dependent mass transfer coefficient was used to model the exchange of PCBs between the pore water and the water column. This coefficient was established from matched water column and sediment PCB data.

It varied from about 3 cm/d in winter to 12 cm/d in early summer. PCBs entering from upstream were estimated from an extensive database of water column PCB and flow measurements extending from 1977 to 1998

Figure 6-6 compares temporal profiles of calculated and observed average PCB<sub>3+</sub> (PCBs with 3 or more chlorine atoms) concentrations in surface (0-5 cm) cohesive and non-cohesive sediments of the Thompson Island Pool, a six-mile reach just downstream of the General Electric facilities that were the original sources of the PCBs. Cohesive sediment PCB<sub>3+</sub> levels decline from 105 ppm in 1977 to 20 ppm in 1991 and 14 ppm in 1998., declines of 80 and 87%, respectively. The model closely reproduces this trend, predicting 18 ppm in 1991 and 10 ppm in 1998, declines of 83 and 90%, respectively. The concentrations computed by the model lie within the uncertainty bars shown on the plot, which indicate  $\pm$  two standard errors of the mean. Thus, there is no statistically significant difference between the model and the data.

The non-cohesive sediment PCB<sub>3+</sub> levels declined from 40 ppm in 1977 to 12 ppm in 1991 and 7 ppm in 1998, declines of 70 and 83% respectively. This downward trend is slower than that of the cohesive sediments. The model reproduces the trend, computing concentrations of 11 ppm in 1991 and 8 ppm in 1998. Thus, the model accounts for the difference in the trend between the cohesive and non-cohesive sediments, as well as the absolute concentration drops between 1977 and 1998.

## **5.2 Subsurface Biochemical Transport Models**

Subsurface biochemical transport models describe the movement and degradation of contaminants in aquifers. These models can be valuable tools in the evaluation of natural remediation and in the predictions of risks associated with contaminants found in aquifer ecosystems. To the casual observer, modeling subsurface natural remediation may appear simple in comparison to modeling natural remediation processes in surface water environments.

However, while there are typically fewer processes to be accounted for in subsurface ecosystems (e.g. insignificant sediment transport), the underground systems are difficult to characterize with regard to distributions of geologic stratigraphy and its effects of water flow and contaminant transport.

A typical subsurface natural remediation-modeling task would involve two distinct modeling steps: 1) groundwater flow modeling, and 2) reactive contaminant transport modeling. In some field sites, the transport and reaction of some system components might significantly modify the properties of porous media itself. For example, the introduction of oxygen into a zone of reduced iron may cause rapid precipitation of oxidized iron during the initiation of an active bioremediation effort. This precipitation event within the aquifer might grossly reduce the permeability and porosity of the porous media. However, for most natural remediation modeling applications, the flow and reactive transport may be considered as uncoupled processes.

### **5.2.1 Modeling Groundwater Flow**

The subsurface groundwater flow system is dynamically linked to the hydrological cycle through various natural or artificial recharge processes. As part of the hydrological cycle, groundwater is



always in motion from regions of recharge to discharge points such as lakes, rivers, or oceans. The role of a groundwater flow model is to characterize the balance of withdrawal or recharge events so that changes in local groundwater flow rates and changes in water levels can be predicted.

In 1856, Henry Darcy performed experimental investigations on the flow of water through homogeneous saturated porous media and formulated the Darcy formula (Bear, 1979). This formula is the basic law that governs the flow of water through porous media. When combined with a mass balance on water, the Darcy formula creates the basis of the groundwater flow model. It should be noted that Darcy's law is not applicable for both saturated and unsaturated groundwater flow systems. However, in this work only saturated flow will be reviewed because many natural remediation modeling applications involve prediction of plume fate in the saturated groundwater region.

Substituting the Darcy formula into the fluid mass balance equation and performing water balance around a control volume, the partial differential equation that governs the flow of groundwater in multi-dimensional saturated porous media can be written as (Freeze and Cherry, 1979; Domenico and Schwartz, 1990):

$$S_s \frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left( K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_y \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_z \frac{\partial h}{\partial z} \right) + q_s \quad (1)$$

where  $h$  is the hydraulic head [L],  $S_s$  is the specific storage coefficient [ $L^{-1}$ ],  $q_s$  is the fluid sink/source term, and  $K_x$ ,  $K_y$ , and  $K_z$  are the principal components of the hydraulic conductivity [ $LT^{-1}$ ]; it is assumed that the aquifer is represented by a orthogonal coordinate systems whose

axis directions are aligned along the principal direction of hydraulic conductivity. The distribution of groundwater head,  $h(x, y, z, t)$  in a specified flow domain is obtained by solving (1) with appropriate initial and boundary conditions. From the hydraulic head distribution, transport velocity field can be estimated using the expression:

$$v_i = -\frac{K_{ii}}{\phi} \frac{\partial h}{\partial x_i} \quad (1)$$

Where  $v$  is the groundwater transport velocity [ $LT^{-1}$ ] and  $\phi$  is the matrix porosity.

Analytical models may be used for solving (1) for specific initial and boundary conditions (Bear, 1979). However, analytical models usually have limited applications because they are usually derived for a specific set of conditions. Several general-purpose finite-element and finite difference codes are available for solving (1) under various initial and boundary conditions. Among available public domain groundwater flow computer codes, MODFLOW (McDonald and Harbaugh, 1988) is the most widely used code. Several pre-and-post processing Graphic-User Interfaces (GUI) are available for the MODFLOW code [e.g. GMS (<http://www.ecgl.byu.edu/software/gms/gms.html>), VisualModflow (<http://www.golden.net/~whs/>), Groundwater vistas (<http://www.groundwatermodels.com/>)] which help in integrating the conceptual site models within MODFLOW's numerical modeling framework. Hence the MODFLOW computer code seems to be one of the feasible alternatives for investigating the groundwater flow distribution at a natural remediation field site.

### 5.2.2 Modeling Reactive Transport

Use of deterministic, single species, advection-dispersion models for analyzing simple reactions

in porous media has been well documented in the literature. The single-species models are relatively simple and, in some special cases, are amenable to analytical solutions (Bear, 1979). Several public-domain computer codes are also available for modeling field-scale transport in natural porous media (Konikow and Bredehoeft, 1978; Voss, 1984; Zheng, 1990). However, none of these codes are capable of simulating coupled, multi-species, reactive transport, especially when the reactions are mediated by complex microbial systems.

Multi-species, bioreactive transport in one-dimensional soil columns has been numerically modeled by other researchers (Molz et al., 1986; Zysset et al., 1994; Clement et al., 1996a; Clement et al., 1997). Chilakapati (1995) presents details of a three-dimensional code for modeling reactive transport in a rectangular domain. de Blanc et al. (1996) modified the multi-phase code, UTCHEM, to model multi-species bioreactive transport. Waddill et al. (1996) present a two-dimensional sequential electron acceptor model for modeling bioremediation of LNAPL-contaminated aquifers. Steefel and Yabusaki present a multi-dimensional code, OS3D, for modeling multi component reactive transport in groundwater systems. Steefel and MacQuarrie present an excellent review of different numerical approaches available for modeling reactive transport in porous media.

In the bioremediation area, Rifai et al. (1987) were the first to present a multi-dimensional model for analyzing the natural fate and transport of hydrocarbon plumes in subsurface environments. This pioneering effort produced a practical computer code, BIOPLUME-II, for analyzing field-scale bioremediation scenarios. BIOPLUME-II uses a modified version of the USGS transport code, MOC, for simulating the two-dimensional reactive transport of fuel-hydrocarbon and

oxygen plumes. The code was recently updated to BIOPLUME-III which allows for simulation of alternate electron acceptors such as nitrate, iron, and sulfate, for fuel hydrocarbon destruction (Rifai et al. 1998). Although these modifications will be useful, the code still has limited applicability because, in BIOPLUME, depth-averaged two-dimensional transport is assumed, bacterial growth is neglected, and only hydrocarbon kinetics are considered. Clement (1998) recently developed a more comprehensive three-dimensional reactive transport model, RT3D, that alleviates several of these practical limitations. Application of the code for several contaminant transport problems is discussed in Clement et al. (1998). RT3D solves the coupled partial differential equations that describe reactive-flow and transport of multiple mobile and/or immobile species in three-dimensional saturated groundwater systems. RT3D is a generalized multi-species version of the U.S. EPA transport code, MT3D (Zheng, 1990). The current version RT3D uses the advection and dispersion solvers from the DOD\_1.5 (1997) version of MT3D.

The general macroscopic equations solved by the RT3D computer code are written as:

$$\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C_k}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C_k) + \frac{q_s}{\phi} C_{s_k} + r_c - r_a + r_d, \text{ where } k = 1, 2, \dots, m \quad (2)$$

$$\frac{d\tilde{C}_{im}}{dt} = \tilde{r}_c + r_a - r_d, \text{ where, } im = 1, 2, \dots, (n - m) \quad (3)$$

where  $n$  is the total number of species,  $m$  is the total number of aqueous-phase (mobile) species (thus,  $n$  minus  $m$  is the total number of solid-phase or immobile species),  $C_k$  is the aqueous-phase concentration of the  $k^{\text{th}}$  species [ $\text{ML}^{-3}$ ],  $\tilde{C}_{im}$  is the solid-phase concentration of the  $im^{\text{th}}$  species [ $\text{MM}^{-1}$ ],  $D_{ij}$  is the hydrodynamic dispersion coefficient [ $\text{L}^2\text{T}^{-1}$ ],  $v$  is the pore velocity [ $\text{LT}^{-1}$ ],  $q_s$  is the volumetric flux of water per unit volume of aquifer representing sources and sinks [ $\text{T}^{-1}$ ]

<sup>1</sup>],  $C_s$  is the concentration of source/sink [ $\text{ML}^{-3}$ ],  $r_c$  is the reaction rate that describes the mass of the species removed or produced per unit volume per unit time [ $\text{ML}^3\text{T}^{-1}$ ],  $\tilde{r}_c$  is the reaction rate at the solid phase [ $\text{MM}^{-1}\text{T}^{-1}$ ], and  $r_a$  and  $r_d$ , respectively, are attachment (or adsorption) and detachment (or desorption) rates that describe the kinetic exchange of the transported species between aqueous and solid phases [ $\text{ML}^{-3}\text{T}^{-1}$ ].

### 5.2.3 Numerical Solution Procedure

RT3D code was developed to solve the multi-species reactive transport equations (2) and (3). The code utilizes a reaction Operator-Split (OS) numerical strategy to solve any number of coupled transport equations [of the form (2) and (3)]. Previously, Walter et al. (1994) have successfully used a similar OS approach to solve multi-component transport with geochemical reactions. Clement et al. (1996a) used the OS strategy to solve a biologically reactive flow problem in a radial system. Valocchi and Malmstead (1992) and Kaluarachchi and Morshed (1995) have noted that splitting the reaction terms using the standard OS strategy may have numerical limitations. They recommended an improved alternating OS strategy that may yield more accurate numerical results. However, Barry et al. (1995) states that the improvement provided by the alternating OS may not be applicable for multi-component nonlinear problems. They also demonstrated the efficiency of the standard OS approach by solving a two species reactive transport problem. In this work, we use a standard OS strategy, similar to the one used by Zheng (1990), to develop a general numerical solution scheme for solving the coupled partial/ordinary differential equations (2) and (3).

Employing the OS strategy, first the mobile species transport equation (2) is divided into four

distinct equations: the advection equation,

$$\frac{\partial C}{\partial t} = - \frac{\partial(v_i C)}{\partial x_i} \quad (4)$$

dispersion equation,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C}{\partial x_j} \right) \quad (5)$$

source/sink-mixing equation,

$$\frac{\partial C}{\partial t} = \frac{q_s}{\phi} C_s \quad (6)$$

and, reaction equation,

$$\frac{dC}{dt} = r \quad (7)$$

where, the term  $r$  represents all possible reaction terms that appear in a typical mobile-species transport equation. Note in a typical immobile species equation [of the form (3)], the advection, dispersion, and source-sink mixing terms are zero and only the reaction term exists.

The USEPA code MT3D uses a similar operator-split approach to solve a mathematical model of the form equation (2) that describes single-species transport with first-order reaction (Zheng, 1990). MT3D is coded into four different packages, each of which is used to sequentially solve the advection equation (5), dispersion equation (6), source-sink mixing equation (7), and single-species reaction equation (8). The advection package has the method of characteristics, modified method of characteristics, hybrid method of characteristics, and upstream finite-difference solution schemes (Zheng, 1990). The dispersion and source-sink mixing packages use explicit finite-difference approximations. RT3D utilizes all the original transport routines available in

MT3D for solving the advection-dispersion problem. The routines are invoked by RT3D multiple times to compute the transport of multiple mobile species. The original MT3D-reaction solver (an explicit solver) was replaced by a new reaction module that has an improved implicit reaction solver. Appropriate code modifications were also implemented to input multiple initial-and-boundary conditions and the multi-species reaction information.

The logical steps involved in the numerical solution procedure are illustrated in Figure 6-7. As shown in Figure 6-7, the use of the operator-split strategy helps solve the complex coupled reactive transport system in a modular fashion. The solution algorithm initially solves the advection, dispersion and source-sink mixing steps for all mobile components for a transport time step  $\Delta t$ . The length of transport step is restricted by the constraints posed from the advection, dispersion, and source-sink mixing solvers (Zheng, 1990). After solving the transport, the coupled reaction equations are solved implicitly by using multiple reaction-time steps. Computation of the required reaction-time step sizes to precisely integrate the differential equations is automated within the differential equation solver. Use of this modular operator-split approach for solving the reactive transport problem facilitates representation of different contaminant transport systems through a set of pre-programmed reaction packages. Further, other user-defined reaction kinetics may also be easily incorporated into the simulator using a user-defined reaction package (Clement, 1998). Currently, the RT3D computer code supports seven reaction packages for modeling different types of reactions (Clement, 1998; Clement and Jones, 1998). Details of several of these reaction packages, which could be used for natural remediation modeling purposes, are described below.

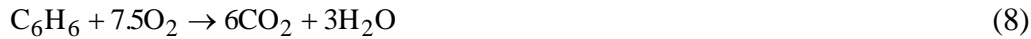
## **5.2.4 Modeling Natural Remediation of Fuel Hydrocarbon Plumes**

**5.2.4.1 Modeling Fuel Hydrocarbon Degradation via Aerobic Processes.** It has been well established that the subsurface microorganisms have the inherent capability to degrade hydrocarbon compounds under aerobic conditions (Borden and Bedient, 1986; Rifai et al., 1988; Chiang et al., 1989). Two conceptual models are available for modeling the subsurface aerobic biodegradation process. The first approach (Borden and Bedient, 1986) simplifies the governing equations by assuming instantaneous reaction between electron donor (BTEX) and the electron acceptor (e.g. oxygen). The instantaneous reaction model assumes that the microbial kinetics have no effect on contaminant concentrations, and the biodegradation is limited only by the transport of oxygen into the contaminant plume. Thus, all available oxygen in an aquifer will be completely depleted in high contaminant regions, and all contaminants will be degraded in high oxygen regions. The presence of low levels of oxygen in high-contaminant regions have been observed in several field sites (Chiang et al., 1987; Rifai et al., 1988; Wiedemeier et al., 1995). In the second model uses a dual-substrate Monod kinetic formulation to calculate biodegradation (Molz et al., 1986; Borden and Bedient, 1986; Rifai et al., 1990; Clement et al., 1996a). In this model biodegradation of contaminants is assumed to be limited by microbial growth kinetics and/or utilization rates.

**Instantaneous Aerobic Reaction Model.** The RT3D computer code has a 2-component instantaneous reaction model that could be used for simulating the aerobic degradation of BTEX. The modeling methodology used is similar the approach used in the BIOPLUME-II (Rifai et al., 1987) code. The method simulates the instantaneous degradation of fuel hydrocarbons under



aerobic conditions described by the reaction:



The transport equations solved by this model are:

$$R_{\text{HC}} \frac{\partial[\text{HC}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{HC}]}{\partial x_j} \right) - \frac{\partial(v_i[\text{HC}])}{\partial x_i} + \frac{q_s}{\phi} [\text{HC}]_s + r_{\text{HC}} \quad (9)$$

$$R_{\text{O}_2} \frac{\partial[\text{O}_2]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{O}_2]}{\partial x_j} \right) - \frac{\partial(v_i[\text{O}_2])}{\partial x_i} + \frac{q_s}{\phi} [\text{O}_2]_s + r_{\text{O}_2} \quad (10)$$

The following algorithm dictates the instantaneous removal rate of either the fuel contaminant or the oxygen (Rifai et al., 1988):

$$HC(t+1) = HC(t) - O(t)/F \text{ and } O(t+1) = 0, \text{ when } HC(t) > O(t)/F \quad (11)$$

$$O(t+1) = O(t) - HC(t) \cdot F \text{ and } HC(t+1) = 0, \text{ when } O(t) > HC(t) \cdot F \quad (12)$$

where, t refers to a particular time step and F is the stoichiometric ratio. Given this algorithm, either the hydrocarbon or the oxygen concentration in a given grid cell will be reduced to zero at each time step, depending on which component is stoichiometrically limiting in the prior time step.

**Dual-Monod Kinetic Model.** To simulate the rate limited degradation of BTEX, the dual-Monod kinetic model available in the RT3D code may be used (Clement et al., 1998). This model provides a general description for simulating reactions between any electron donor and electron acceptor mediated by actively growing bacteria that live in both aqueous and soil phases. Application of similar types of double-Monod models are discussed by: Molz et al. (1986); Rifai and Bedient (1990); Tayler and Jaffe (1990); Clement et al. (1996a); Clement et al.

(1996b); Reddy et al. (1997); Clement et al. (1997b); and Clement et al. (1998).

Assuming an equilibrium model for sorption and a Monod kinetic model for biological reactions (Rifai and Bedient 1990; Clement et al. 1996a), the fate and transport of an electron donor (e.g. a hydrocarbon) in a multi-dimensional saturated porous media can be written as:

$$R_D \frac{\partial [D]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [D]}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i [D]) + \frac{q_s}{\phi} [D_s] - \mu_m \left( [X] + \frac{\rho \tilde{X}}{\phi} \right) \left( \frac{[D]}{K_D + [D]} \right) \left( \frac{[A]}{K_A + [A]} \right) \quad (13)$$

where  $[D]$  is the electron donor concentration in the aqueous phase  $[ML^{-3}]$ ,  $[D_s]$  is the donor concentration in the sources/sinks  $[ML^{-3}]$ ,  $D_{ij}$  is the dispersion tensor;  $[X]$  is the aqueous phase bacterial cell concentration  $[ML^{-3}]$ ,  $\tilde{X}$  is the solid-phase cell concentration (mass of bacterial cells per unit mass of porous media  $[MM^{-1}]$ ),  $[A]$  is the electron acceptor concentration in the aqueous phase  $[ML^{-3}]$ ,  $R_H$  is the retardation coefficient of the hydrocarbon,  $K_D$  is the half saturation coefficient for the electron donor  $[ML^{-3}]$ ,  $K_A$  is the half saturation coefficient for the electron acceptor  $[ML^{-3}]$ , and  $\mu_m$  is the contaminant utilization rate  $[T^{-1}]$ . The model assumes that the degradation reactions occur only in the aqueous phase, which is usually a conservative assumption.

The fate and transport of the electron acceptor (e.g. oxygen) can be modeled using the equation:

$$R_A \frac{\partial [A]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [A]}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i [A]) + \frac{q_s}{\phi} [A_s] - Y_{A/D} \mu_m \left( [X] + \frac{\rho \tilde{X}}{\phi} \right) \left( \frac{[D]}{K_D + [D]} \right) \left( \frac{[A]}{K_A + [A]} \right) \quad (14)$$

where  $Y_{A/D}$  is the stoichiometric yield coefficient, and  $R_A$  is the retardation coefficient of the electron acceptor.

The fate and transport of bacteria in the aqueous phase can be described using the equation:

$$\frac{\partial[X]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[X]}{\partial t} \right) - \frac{\partial}{\partial x_i} (v_i[X]) + \frac{q_s}{\phi} [X_s] - K_{att}[X] + \frac{K_{det}\rho\tilde{X}}{\phi} + Y_{X/D} \mu_m [X] \left( \frac{[D]}{K_D + [D]} \right) \left( \frac{[A]}{K_A + [A]} \right) - K_e[X] \quad (15)$$

where  $K_{att}$  is the bacterial attachment coefficient [ $T^{-1}$ ],  $K_{det}$  is the bacterial detachment coefficient [ $T^{-1}$ ], and  $K_e$  is the endogenous cell death or decay coefficient [ $T^{-1}$ ].

The growth of attached-phase bacteria can be described using an ordinary differential equation of the form:

$$\frac{d\tilde{X}}{dt} = \frac{K_{att}\phi[X]}{\rho} - K_{det}\tilde{X} + Y_{X/D} \mu_m \tilde{X} \left( \frac{[D]}{K_D + [D]} \right) \left( \frac{[A]}{K_A + [A]} \right) - K_e\tilde{X} \quad (16)$$

The conceptual model for representing soil bacteria, implicitly assumed in the above formulation is similar to the macroscopic model described by Baveye and Valocchi (1989); no specific microscopic biomass structure is assumed, and diffusional limitations across biofilm are also neglected. Equations (15) and (16) also assume first-order kinetic expressions for representing the exchange of bacteria cells between aqueous and solid phases (Taylor and Jaffe, 1990; Hornberger et al. 1992; Peyton et al. 1995). More recently, Reddy and Ford (1996) compared equilibrium and kinetic expressions for modeling the microbial exchange process and concluded that kinetic models provide more general description. Permeability and porosity changes caused by bacterial growth are ignored in this formulation. However, if required, macroscopic models

for biomass-affected porous-media properties, described in Clement et al. (1996b), may be integrated within this modeling approach.

#### **6.2.4.2 Modeling Fuel Hydrocarbon Decay via Aerobic and Anaerobic Processes utilizing**

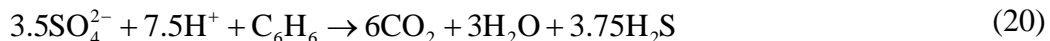
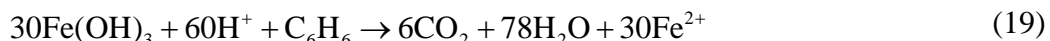
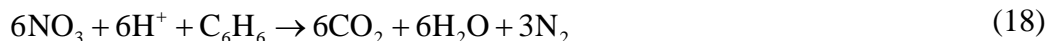
**Multiple Electron Acceptors.** Over the past two decades, numerous laboratory and field studies have shown that microorganism indigenous to subsurface environment can degrade fuel hydrocarbon under both aerobic and anaerobic conditions (Wiedemeier et al., 1995). During biodegradation, microorganisms transform available carbon into forms useful for energy and cell production. This results in oxidation of the electron donor and reduction of electron acceptor. Electron donors include natural organic matter and anthropogenically introduced carbon, such as fuel hydrocarbon. Electron acceptors are elements or compounds that occur in relatively oxidized states. The more common electron acceptors in groundwater include dissolved oxygen, nitrate, iron(III), sulfate, and carbon dioxide. The electron acceptors are listed in the expected sequence that is established based on the Gibb's free energy of the redox reactions.

In literature, three approaches are described for modeling the fuel-degradation process coupled to multiple electron acceptors. The first approach is a simple extension of two-component instantaneous reaction modeling approach (Rifai et al., 1998). The instantaneous reaction algorithm originally derived for single electron acceptor (oxygen) is simply extended to describe multiple electron acceptors. The second approach is used a first-order kinetic model to describe various reaction rates (Clement et al., 1997). The rate constants are assumed to be first-order with respect to hydrocarbon and a rate-limiting term and an inhibition term, respectively, are used to simulate the presence and absence of different electron acceptors. The third approach

uses a detailed Monod-kinetic model where the kinetics of each individual microbial population is tracked in detail to describe various reactions (Waddill et al., 1996). This multi-population kinetic dependency concept is numerically more complex to simulate. It also requires extensive field data to support and hence very little work has been done in applying such model to a field scale. Moreover, for easily degradable contaminants such as fuel hydrocarbons, which found to degrade ubiquitously, such detailed modeling efforts may not be required. Therefore, in the section below we only discuss the first two approaches in detail and show how they are included within the RT3D computer code's reactive transport modeling framework.

**Instantaneous Reaction Model for Fuel Hydrocarbon Decay Utilizing Multiple Electron**

**Acceptors.** To simulate degradation of fuel hydrocarbon using multiple electron acceptors, a 6-component, instantaneous reaction model has been developed. This model simulates the instantaneous degradation of fuel-hydrocarbon based on following chemical reactions:



The reaction rates are assumed to occur in a sequential order, as listed above, and the reaction rates are assumed to be instantaneous. Since the iron reduction capacity (or the bioavailable concentration of  $\text{Fe}^{3+}$ ) and the methanogenic capacity (MC) are not readily quantifiable under

normal field conditions, these processes are represented by “assimilative capacity terms” for iron reduction and methanogenesis, defined as:

$$[\text{Fe}^{3+}] = [\text{Fe}^{2+}_{\text{max}}] - [\text{Fe}^{2+}] \quad (22)$$

$$[\text{MC}] = [\text{CH}_{4,\text{max}}] - [\text{CH}_4] \quad (23)$$

where  $[\text{Fe}^{2+}_{\text{max}}]$  and  $[\text{CH}_{4,\text{max}}]$  are the maximum measured aquifer levels of these species that represent aquifer’s (maximum) capacity for iron reduction and methanogenesis, respectively.

The couple set of transport equations that describe the transport of all six reacting species can be written as:

$$R_{\text{HC}} \frac{\partial[\text{HC}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{HC}]}{\partial x_j} \right) - \frac{\partial(v_i[\text{HC}])}{\partial x_i} + \frac{q_s}{\phi} [\text{HC}]_s + r_{\text{HC}} \quad (24)$$

$$R_{\text{O}_2} \frac{\partial[\text{O}_2]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{O}_2]}{\partial x_j} \right) - \frac{\partial(v_i[\text{O}_2])}{\partial x_i} + \frac{q_s}{\phi} [\text{O}_2]_s + r_{\text{O}_2} \quad (25)$$

$$R_{\text{NO}_3} \frac{\partial[\text{NO}_3]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{NO}_3]}{\partial x_j} \right) - \frac{\partial(v_i[\text{NO}_3])}{\partial x_i} + \frac{q_s}{\phi} [\text{NO}_3]_s + r_{\text{NO}_3} \quad (26)$$

$$R_{\text{Fe}^{2+}} \frac{\partial[\text{Fe}^{2+}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{Fe}^{2+}]}{\partial x_j} \right) - \frac{\partial(v_i[\text{Fe}^{2+}])}{\partial x_i} + \frac{q_s}{\phi} [\text{Fe}^{2+}]_s + r_{\text{Fe}^{2+}} \quad (27)$$

$$R_{\text{SO}_4} \frac{\partial[\text{SO}_4]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{SO}_4]}{\partial x_j} \right) - \frac{\partial(v_i[\text{SO}_4])}{\partial x_i} + \frac{q_s}{\phi} [\text{SO}_4]_s + r_{\text{SO}_4} \quad (28)$$

$$R_{\text{CH}_4} \frac{\partial[\text{CH}_4]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{CH}_4]}{\partial x_j} \right) - \frac{\partial(v_i[\text{CH}_4])}{\partial x_i} + \frac{q_s}{\phi} [\text{CH}_4]_s + r_{\text{CH}_4} \quad (29)$$

The removal term  $r$  is computed using an instantaneous reaction model similar to the one used for modeling the aerobic instantaneous reaction. The following general algorithm is used for

computing either the removal of either the electron donor (D) or the electron acceptor (A) within a reaction time step:

$$D(t+1) = D(t) - A(t)/F \text{ and } A(t+1) = 0, \text{ when } D(t) > A(t)/F \quad (30)$$

$$A(t+1) = A(t) - D(t) \cdot F \text{ and } D(t+1) = 0, \text{ when } A(t) > D(t) \cdot F \quad (31)$$

where, t refers to a particular time step and F is the stoichiometric ratio and its values are 3.08, 4.77, 21.5, 4.6, and 0.78, respectively, for the reactions (17) to (21).

**First-Order Kinetic Model for Fuel Hydrocarbon Decay utilizing Multiple Electron Acceptors.** The kinetic model considered here describes rate-limited degradation of hydrocarbon through five distinct degradation pathways. Similar to the previous model, this model also describes sequential degradation of fuel hydrocarbon under aerobic, denitrifying, iron-reducing, sulfate-reducing, and methanogenic conditions. The transport system solved is exactly similar to the system described by equations (24) to (29). However, the kinetics of hydrocarbon decay are assumed to be first order with respect to hydrocarbon concentration. A Monod-type term is used to account for the presence (or the absence) of various electron acceptors, and an inhibition model is used to describe sequential utilization of various electron acceptors. The following kinetic framework is used to represent degradation of hydrocarbon through different electron acceptor pathways:

$$r_{\text{HC},\text{O}_2} = -k_{\text{O}_2} [\text{HC}] \frac{[\text{O}_2]}{K_{\text{O}_2} + [\text{O}_2]} \quad (32)$$

$$r_{\text{HC},\text{NO}_3} = -k_{\text{NO}_3} [\text{HC}] \frac{[\text{NO}_3]}{K_{\text{NO}_3} + [\text{NO}_3]} \frac{K_{i,\text{O}_2}}{K_{i,\text{O}_2} + [\text{O}_2]} \quad (33)$$

$$r_{\text{HC,Fe}^{2+}} = -k_{\text{Fe}^{3+}} [\text{HC}] \frac{[\text{Fe}^{3+}]}{K_{\text{Fe}^{3+}} + [\text{Fe}^{3+}]} \frac{K_{i,\text{O}_2}}{K_{i,\text{O}_2} + [\text{O}_2]} \frac{K_{i,\text{NO}_3}}{K_{i,\text{NO}_3} + [\text{NO}_3]} \quad (34)$$

$$r_{\text{HC,SO}_4} = -k_{\text{SO}_4} [\text{HC}] \frac{[\text{SO}_4]}{K_{\text{SO}_4} + [\text{SO}_4]} \frac{K_{i,\text{O}_2}}{K_{i,\text{O}_2} + [\text{O}_2]} \frac{K_{i,\text{NO}_3}}{K_{i,\text{NO}_3} + [\text{NO}_3]} \frac{K_{i,\text{Fe}^{3+}}}{K_{i,\text{Fe}^{3+}} + [\text{Fe}^{3+}]} \quad (35)$$

$$r_{\text{HC,CH}_4} = -k_{\text{CH}_4} [\text{HC}] \frac{[\text{CO}_2]}{K_{\text{CH}_4} + [\text{CO}_2]} \frac{K_{i,\text{O}_2}}{K_{i,\text{O}_2} + [\text{O}_2]} \frac{K_{i,\text{NO}_3}}{K_{i,\text{NO}_3} + [\text{NO}_3]} \frac{K_{i,\text{Fe}^{3+}}}{K_{i,\text{Fe}^{3+}} + [\text{Fe}^{3+}]} \frac{K_{i,\text{SO}_4}}{K_{i,\text{SO}_4} + [\text{SO}_4]} \quad (36)$$

where  $r_{\text{HC,O}_2}$  is the rate at which hydrocarbon is destroyed by utilizing oxygen,  $r_{\text{HC,NO}_3}$  is the destruction rate utilizing nitrate,  $r_{\text{HC,Fe}^{2+}}$  is the destruction rate utilizing  $\text{Fe}^{3+}$  (or producing  $\text{Fe}^{3+}$ ),  $r_{\text{HC,SO}_4}$  is the destruction rate utilizing sulfate,  $r_{\text{HC,CH}_4}$  is the destruction rate via methane production,  $[\text{O}_2]$  is oxygen concentration  $[\text{ML}^{-3}]$ ,  $k_{\text{O}_2}$  is the first-order rate constant  $[\text{T}^{-1}]$ ,  $K_{\text{O}_2}$  is the Monod half saturation constant  $[\text{ML}^{-3}]$  (note by pre-setting the half-saturation constants to a small value we can simulate zero-order dependency with respect electron donor, and hence a first-order degradation model with respect to hydrocarbon), and  $K_{i,\text{O}_2}$  is the oxygen inhibition constant  $[\text{ML}^{-3}]$ ; similar nomenclature was used for all other reactions.

Since methane production is a fermentation process, there is no external electron transfer process involved in this reaction step. Therefore, the concentration term for  $\text{CO}_2$ , used in (36) and (23), should be considered as a hypothetical term that simply indicates the Methanogenic Capacity (MC) of the aquifer. Similarly, the concentration term for  $\text{Fe}^{3+}$  should also be considered as a



hypothetical term that simply indicates the iron reduction capacity of the aquifer. Using the transformation equations (22) and (23), the unquantifiable concentration levels of the species  $\text{Fe}^{3+}$  and  $\text{CO}_2$  (or MC) are related back to field-measurable  $\text{Fe}^{2+}$  and  $\text{CH}_4$  concentration levels.

Since the concentrations of  $\text{Fe}^{3+}$  and  $\text{CO}_2$  are hard to quantify, the transformation equations (22) and (23) are used to relate the concentration levels of the species  $\text{Fe}^{3+}$  and  $\text{CO}_2$  (or MC) back to field-measurable  $\text{Fe}^{2+}$  and  $\text{CH}_4$  concentration levels.

The total rate of hydrocarbon destruction is given as:

$$r_{\text{HC}} = r_{\text{HC},\text{O}_2} + r_{\text{HC},\text{NO}_3} + r_{\text{HC},\text{Fe}^{2+}} + r_{\text{HC},\text{SO}_4} + r_{\text{HC},\text{CH}_4} \quad (37)$$

Rates of electron acceptor utilization are given as the corresponding rate of hydrocarbon destruction multiplied by the appropriate yield coefficients (Y):

$$r_{\text{O}_2} = Y_{\text{O}_2/\text{HC}} r_{\text{HC},\text{O}_2} \quad (38)$$

$$r_{\text{NO}_3} = Y_{\text{NO}_3/\text{HC}} r_{\text{HC},\text{NO}_3} \quad (39)$$

$$r_{\text{Fe}^{2+}} = -Y_{\text{Fe}^{2+}/\text{HC}} r_{\text{HC},\text{Fe}^{2+}} \quad (40)$$

$$r_{\text{SO}_4} = Y_{\text{SO}_4/\text{HC}} r_{\text{HC},\text{SO}_4} \quad (41)$$

$$r_{\text{CH}_4} = -Y_{\text{CH}_4/\text{HC}} r_{\text{HC},\text{CH}_4} \quad (42)$$

The default value set for all the half-saturation constants is 0.5 mg/L, and for all the inhibition constants is 0.01 mg/L. Assuming BTEX to represent all fuel contaminants, the yield value for  $Y_{\text{O}_2/\text{HC}}$  is 3.14,  $Y_{\text{NO}_3/\text{HC}}$  is 4.9,  $Y_{\text{Fe}^{2+}/\text{HC}}$  is 21.8,  $Y_{\text{SO}_4/\text{HC}}$  is 4.7, and  $Y_{\text{CH}_4/\text{HC}}$  is 0.78.

### 5.2.5 Modeling Natural Remediation of Chlorinated Solvents Plumes

Waste sites where chlorinated solvent plumes are of primary concern commonly exist throughout

North America. Most of these chlorinated solvent plumes originated from waste disposal pits where industrial solvents, such as PCE (tetrachloroethylene) and TCE (trichloroethylene) were indiscriminately disposed. Recent demonstrations of natural degradation of petroleum hydrocarbon, in virtually all groundwater systems, have raised the prospects that chlorinated solvents might also be amenable for natural remediation. Wiedemeier et al. (1997) presented a technical protocol that documents the conditions under which natural remediation of chlorinated solvent may be feasible. The degree of natural remediation will obviously depend on the biodegradation potential of the aquifer. Based on previous lab and field-scale results, they report that the representative first-order biodegradation rates for chlorinated solvents in the presence of aquifer materials may range from 0.00068 to 0.54 day<sup>-1</sup> for PCE, 0.0001 to 0.021 day<sup>-1</sup> for TCE, 0.00016 to 0.026 day<sup>-1</sup> for DCE, and 0.0003 to 0.012 day<sup>-1</sup> for VC (Wiedemeier et al. 1997).

Numerous field and laboratory studies have demonstrated that microorganisms can degrade chlorinated solvents (Bower et al., 1981; Freeman and Gossett, 1989; Semprini et al., 1995; Klier et al., 1998). The most important process for the natural degradation of the more highly chlorinated solvents is the anaerobic reductive dehalogenation process (Wiedemeier et al., 1997).

During this process, the chlorinated solvent is used as an electron acceptor and chlorine atoms are sequentially removed and replaced with hydrogen atoms. Under favorable environmental conditions, other biochemical processes, in addition to anaerobic decay, may also degrade the chlorinated organics. McCarty and Semprini (1994) indicate that dichloro- and mono-chloroethenes have a good potential for degradation via both direct or cometabolic aerobic pathways. Based on radio-labeled microcosm studies, Klier et al. (1998) have shown evidences for aerobic dichloroethene degradation. Based on this information, we formulated a conceptual

model for describing all biochemical reaction steps involved in dechlorination of various chlorinated solvent chemicals. In this model, the degradation reactions are assumed to be mediated by both aerobic and anaerobic dechlorination processes, as shown in Figure 6-8.

Assuming first-order biodegradation kinetics for every reaction step, the transport and transformation of PCE, TCE, DCE, VC, ETH, and Cl can be simulated by solving the following set of partial differential equations:

$$R_P \frac{\partial[\text{PCE}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{PCE}]}{\partial x_j} \right) - \frac{\partial(v_i[\text{PCE}])}{\partial x_i} + \frac{q_s}{\phi} [\text{PCE}]_s - K_P[\text{PCE}] \quad (43)$$

$$R_T \frac{\partial[\text{TCE}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{TCE}]}{\partial x_j} \right) - \frac{\partial(v_i[\text{TCE}])}{\partial x_i} + \frac{q_s}{\phi} [\text{TCE}]_s + Y_{T/P} K_P[\text{PCE}] - K_{T1}[\text{TCE}] - K_{T2}[\text{TCE}] \quad (44)$$

$$R_D \frac{\partial[\text{DCE}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{DCE}]}{\partial x_j} \right) - \frac{\partial(v_i[\text{DCE}])}{\partial x_i} + \frac{q_s}{\phi} [\text{DCE}]_s + Y_{D/T} K_T[\text{TCE}] - K_{D1}[\text{DCE}] - K_{D2}[\text{DCE}] \quad (45)$$

$$R_V \frac{\partial[\text{VC}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{VC}]}{\partial x_j} \right) - \frac{\partial(v_i[\text{VC}])}{\partial x_i} + \frac{q_s}{\phi} [\text{VC}]_s + Y_{V/D} K_{D1}[\text{DCE}] - K_{V1}[\text{VC}] - K_{V2}[\text{VC}] \quad (46)$$

$$R_E \frac{\partial[\text{ETH}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{ETH}]}{\partial x_j} \right) - \frac{\partial(v_i[\text{ETH}])}{\partial x_i} + \frac{q_s}{\phi} [\text{ETH}]_s + Y_{E/V} K_{V1}[\text{VC}] - K_{E1}[\text{ETH}] - K_{E2}[\text{ETH}] \quad (47)$$

$$R_C \frac{\partial[\text{Cl}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial[\text{Cl}]}{\partial x_j} \right) - \frac{\partial(v_i[\text{Cl}])}{\partial x_i} + \frac{q_s}{\phi} [\text{Cl}]_s + Y1_{C/P} K_{P1}[\text{PCE}] + Y1_{C/T} K_{T1}[\text{TCE}] \\ + Y1_{C/D} K_{D1}[\text{DCE}] + Y1_{C/V} K_{V1}[\text{VC}] + Y2_{C/T} K_{T2}[\text{TCE}] + Y2_{C/D} K_{D2}[\text{DCE}] \\ + Y2_{C/V} K_{V2}[\text{VC}] \quad (48)$$

where [PCE], [TCE], [DCE], [VC], [ETH], and [Cl] represent contaminant concentrations of various species [mg/L];  $K_P$ ,  $K_{T1}$ ,  $K_{D1}$ , and  $K_{V1}$ , and  $K_{E1}$  are first-order anaerobic degradation rates [ $\text{day}^{-1}$ ];  $K_{T2}$ ,  $K_{D2}$ , and  $K_{V2}$ , and  $K_{E2}$  are first-order aerobic degradation rates [ $\text{day}^{-1}$ ];  $R_P$ ,  $R_T$ ,

$R_D$ ,  $R_V$ ,  $R_E$ , and  $R_C$  are retardation factors;  $Y_{T/P}$ ,  $Y_{D/T}$ ,  $Y_{V/D}$ , and  $Y_{E/V}$  are chlorinated compound yields under anaerobic reductive dechlorination conditions— their values are: 0.79, 0.74, 0.64 and 0.45, respectively;  $Y_{1C/P}$ ,  $Y_{1C/T}$ ,  $Y_{1C/D}$ , and  $Y_{1C/V}$  are yield values for chloride under anaerobic conditions— their values are: 0.21, 0.27, 0.37, and 0.57, respectively; and  $Y_{2C/T}$ ,  $Y_{2C/D}$ , and  $Y_{2C/V}$  are yield values for chloride under aerobic conditions— their values are: 0.81, 0.74, and 0.57, respectively. The yield values are estimated from the reaction stoichiometry and molecular weights. The anaerobic degradation of one mole of PCE would yield one mole of TCE, therefore  $Y_{T/P} = \text{molecular weight of TCE}/\text{molecular weight of PCE}$  ( $131.4/165.8 = 0.79$ ). Note the reaction models presented above assume that the biological degradation reactions only occur in the aqueous phase, which is a conservative assumption.

All the reaction models described in this chapter for modeling natural remediation of fuel-hydrocarbon and chlorinated solvent plumes are available in the RT3D code as pre-programmed reaction modules. Several of these modules are field tested. In addition, several test example data sets for applying these modules to predict plume migration scenarios, within the GMS modeling environment, are documented in Clement and Jones (1998c).

## **Summary**

Natural remediation is the reduction in contaminant concentration that naturally occurs as a result of contaminant diffusion and dispersion, and as a result of natural degradation through biotic and chemical reactions in the environment. This chapter describes important aspects of the use and understanding of numerical models in the evaluation of natural remediation scenarios. For this chapter, natural remediation models have been divided into two broad

classes; surface water models and groundwater models. Each environment, and thus model type, has its own unique characteristics that control the rate of contaminant transport, dilution, and degradation.

Surface water models have four components that must be integrated to produce an accurate representation of contaminant fate and transport. These components are surface water hydrodynamics, sediment transport, contaminant sorption/desorption processes, and contaminant transformations (either biotic or chemical). The hydrodynamics of surface water systems describe processes that affect the movement of water, and subsequently, the movement of soluble and suspended contaminants from one location to another. In these surface water systems, sediment transport is often a critical component of the model since many contaminants are strongly sorbed to sediment particles. The deposition of sediment may significantly slow the spreading of a contaminant. In contrast, resuspension events, such as floods or annual spring runoff, may significantly increase, and may dominate, the contaminant transport properties in surface systems. Contaminant sorption/desorption processes and transformation rates are often very site and contaminant specific. Sorption/desorption processes control the distribution of a contaminant between the solid and aqueous phases of the system. Transformation rates describe the chemical or biological reactions that affect contaminant concentrations. Without laboratory testing the sorption/desorption and reaction parameters are often difficult to quantify. Therefore these processes, though very complex and the subject of significant research, are often modeled as simple equilibrium and first order processes, respectively.

In contrast to surface water modeling, subsurface or groundwater modeling is slightly less

complex because of the significantly lower sediment transport load in aquifer systems and the typically lower level of macrobiotic diversity found in aquifer systems. Natural remediation modeling of groundwater systems requires knowledge of the subsurface hydrodynamics of groundwater flow in response to natural hydrostatic gradients. Groundwater flow patterns can also be influenced by wells used for irrigation or drinking water. Like surface water systems, groundwater contaminant fate and transport is affected by contaminant sorption/desorption and chemical and biotic transformations. Significant research has improved our understanding of the chemical and biological processes that occur naturally in groundwater. These processes can decrease contaminant concentrations and may eventually limit further spreading of contaminant plumes.

Overall, modeling the natural remediation of contaminants in surface and subsurface water systems has the potential to improve our estimates of the degradation rates and the extent of spreading of contaminants released into our environment. In providing these estimates, the real risks associated with natural remediation of environmental contaminants may be better balanced against the costs of other remediation methods.

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## Figures

## Numerical Solution Procedure...

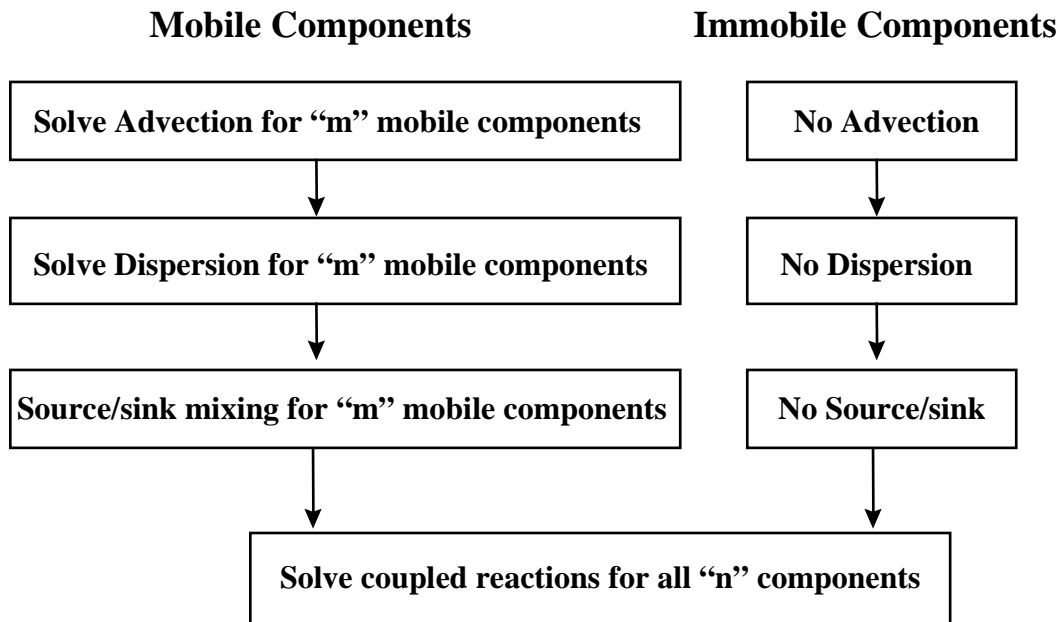


Figure 6-8. Block Diagram Illustrating the Numerical Solution Scheme





# Biogeochemical Model Components

